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# Some Double Chlorides

CONTAINING

# BISMUTH.

A DISSERTATION

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BY

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# CONTENTS.

# Acknowledgment

I desire to offer my most sincere thanks to Professor Remsen at whose suggestion and under whose immediate direction the following investigation has been carried out.

I wish also to thank Doctors Morse and Renouf for valued instruction, and finally Doctor George H Williams under whom the course in mineralogy and geology was pursued.

# Introduction.

It was for a long time held that a sharp line could be drawn separating the oxygen acids and bases, but as experiments have shown, some substances have the power to act in either capacity, depending on the way they are treated.
Chromium for example: when chromium hydroxide is treated with hydrochloric acid, a chloride is formed, with chromium performing the function of a base, while when treated with alkaline hydroxide, a chromite results, here chromium shows acid properties.
Why if basic oxides and acidic oxides unite to form salts, should not the

halides unite to form compounds in keeping in constitution to the double oxides?

Not only, why should they not be formed, but why should they not receive proper places in text books with significant names? thus $K_2O + SO_3 = K_2SO_4$ or potassium sulphate is given in all books as a derivative of the well known sulphuric acid; while a salt formed by potassium chloride and lead chloride is generally disregarded probably because the acid from which it is most likely derived does not exist in the free state, namely chloro-plumbous acid

$KCl + PbCl_2 = KPbCl_3$ or potassium chloro-plumbite

In a paper in Am. Chem.[1] entitled "On the Nature and Structure of the Double

1 Am. Chem. J. 11, 291

Halides". he emphasizes this point — the close similarity between the double oxides or oxygen salts, and the double halides, the act involved in their formation and for their explanation suggests that "two halogen atoms together can play the same part that the so called linking oxygen atoms plays in the oxygen salts" thus:

$$Al\begin{cases} O \\ ONa \end{cases} \qquad\qquad Al\begin{cases} Cl_2 \\ (Cl_2)Na \end{cases}$$

$$Al\begin{cases} O\,Na \\ O\,Na \\ O\,Na \end{cases} \qquad\qquad Al\begin{cases} (Cl_2)Na \\ (Cl_2)Na \\ (Cl_2)Na \end{cases}$$

This view has been held for many years. The same explanation was first offered by Naquet[2] in 1867; he says in the compound of silver chloride and potassium chloride the chlorine acts as a bivalent element and gives it the formula

$$\begin{matrix} Ag \\ K \end{matrix} > \overset{II}{Cl_2}$$

2 Principes de Chimie fondée sur les théories modernes. Par A. Naquet. Paris, 867

Blomstrand[3] 1869 offers a similar explanation for the double chloride of magnesium and potassium and gives this formula

$$Mg < {Cl \atop Cl = Cl\,K}$$

in which he conceives the chlorine atom to be a trivalent element.

Of this view that halogen atoms can play the same part as uniting oxygen atoms, it is easy to see the very close analogy existing between the ordinary oxygen salts and the double halides.

Prof. Remsen, after an exhaustive examination of the composition of this large class of compounds, deduces this law.

"When a halide of any element combines with a halide of an alkali metal to form a double salt, the number of molecules of the alkali salt which are added to one molecule of the other halide is never greater

3 Die Chemie der Jetztzeit vom Standpunkte der electro-chemischen Auffassung aus Berzelius' Lehre entwickelt.

and is generally less than the number of halogen atoms contained in the latter". The principal objection to this view is by Prof. Horstmann[4] and based on the valence of the halogen — that they are univalent — granting this, what would become of the well established compounds $ICl_3$ and $IF_5$? If it be granted that these are true chemical compounds, then the objection of Prof. Horstmann loses force.

A few words regarding the double halides of bismuth and the alkalies will not be out of place in this connection. With potassium the following compounds are recorded.

| | | |
|---|---|---|
| $BiCl_3 \cdot 3KCl$. | Arppe Berzelius Berichte | 25, 279 |
| $BiCl_3 \cdot 2KCl$. | " " " | 25, 279 |
| $BiCl_3 \cdot 2KCl + 2H_2O$ | Jacquelaine Ann. Chim. phys. | 00, 113 |
| $BiI_3 \cdot 2KI + H_2O$ | Arppe Berzelius Jahrsb. | 25, 284 |
| $BiI_3 \cdot 4KI + \dot{H}I$ (?) | " " " | 25, 284 |

4- Lehrbuch der Physikalischen und Theoretischen Chemie von A. Horstmann und H. Landolt.

$BiCl_3 . 2KBr + 1\frac{1}{2} H_2O$ Atkinson J. Chem. Soc. 1883, 292

Of the double potassium-bismuth salts I worked only with the chlorides. The result of this investigation proved the non-existence of the salts $BiCl_3 . 3KCl$ and $BiCl_3 . 2KCl$ obtained by Arppe, while under certain conditions a compound of the composition $BiCl_3 . KCl + H_2O$ was formed, of which I can find no record.

There are recorded many other double halides of bismuth, which are here tabulated with their respective references:

| | | |
|---|---|---|
| $BiCl_3 . 2NaCl + 3H_2O$ | Jacquelaine Ann. chim. phys | 66, 113 |
| $BiCl_3 . NH_4Cl$ | " " " | " 66, 113 |
| $BiCl_3 . 2NH_4Cl$ | Deherain, Compt. rend. | 54, 724 |
| $BiCl_3 . 3NH_4Cl$ | " " " | 54, 724 |
| $BiBr_3 . 3NH_4Cl + H_2O$ | Muir J. Chem. Soc | 1876, 148 |
| $BiBr_3 . 2NH_4Cl + 3H_2O$ | " " " " | 1876, 148 |
| $BiBr_3 . 2NH_4Cl + 5H_2O$ | Hickles " " " | 1876, 148 |

$2BiBr_3 . 5NH_4Cl + H_2O$ Muir J. Chem. Soc. 1877. 28.
Of other double salts of bismuth there are two of the composition
$3K_2SO_4 . Bi_2(SO_4)_3$ Berzelius Jahrsb 25, 280
$2K_2SO_4 . BiO(SO_4)_2$ " " 25 286
I speak of these simply because in a method of analysis employed for the determination of chlorine in the double chloride $BiCl_3 . 2KCl + 2H_2O$ I obtained a salt — a double sulphate — differing in composition from either of the above and mention of which I have been unable to find in the literature.
Godeffroy[5] describes the salts $BiCl_3 . 6RbCl$ and $BiCl_3 . 6CsCl$, which cannot but strike one as being marked exceptions to Prof. Remsen's law. With these facts at hand the following work on the double salts of bismuth chloride with the chlorides of rubidium and

5 Berichte 8, 9 und Zeitschrift des allgemeinen österreichischen Apotheker-Verein

caesium was undertaken to determine whether or not these compounds really exist. At the time Prof. Remsen's article appeared the following salts were found described in the literature and appear as exceptions to the rule

| | | |
|---|---|---|
| $SnCl_2.4KCl+3H_2O$ | Poggiale, J. prakt. Chem. | 35, 329 |
| $CuCl.2KCl$ | Mitscherlich, Ann. chim. phys. | 73, 384 |
| $MnF_2.4KF$ | Nicklès, Bull. Soc. Chim [2] | 8, 408 |
| $PbI_2.4KI$ | Boullay, Ann. chim. phys [2] | 34, 370 |
| $BiCl_3.6RbCl$ | Godeffroy Berichte | 8, 9 |
| $BiCl_3.6CsCl$ | " " | 8, 9 |
| $SbCl_3.6RbCl$ | " " | 8, 9 |
| $SbCl_3.6CsCl$ | " " | 8, 9 |
| $CdCl_2.4KCl$ | von Hauer Wiener Akad. Ber | 15, 23 |

For the past two years work has been carried on along this line, in this laboratory with the most gratifying results, as many of these salts have been shown not to exist.

Mr C. H. Herty[6] has most carefully investigated the double salts of lead and potassium with the results — that none of those salts which appear as exceptions exist, but the compound $KPbI_3 + 2H_2O$ is always formed when lead iodide and potassium iodide are brought together in hydrochloric acid solution.
Mr Geo M. Richardson[7] in his work on the double salts of tin and potassium shows conclusively that the compound $SnCl_2.4KCl + 3H_2O$ as described by Poggiale cannot be obtained.
Mr C. E. Saunders also working in this laboratory has been unable to obtain either of the salts $SbCl_3.6RbCl$ or $SbCl_3.6CsCl$.
Christensen[8] shows that the salt $MnF_2.7KF$ cannot be prepared according to the directions given by Nickles.
With the results of the work described in the following pages, all the exceptions to the law

6 Thesis for Ph.D. degree Johns Hopkins University 1890
7 " " " " " " "
8 J. prakt. Chem " 1886, " 41

have been explained away, save the compounds $CuCl . 2KCl$ and $CdCl_2 . 4KCl$. All work on these latter two points to the correctness of these formulae as expressing their true composition.

## Method of Analysis.

Although Godeffroy in his article gives the results of complete analyses of the different salts described therein, he fails to give the methods employed, which would indicate, to say the least, that they are simple and straightforward; but the work of analysing the double chlorides of bismuth and the alkalies present many difficulties; a few of which I will cite.

Ammonium sulphide (freshly prepared) was added to the double salt to which water had previously been added — thus precipitated the bismuth, which was filtered off on a washed filter, washed with water containing a little hydrogen sulphide, dried in an air

bath at 90°, scraped into a weighed porcelain crucible (the filter afterwards ecinit) and treated with a few drops of C.P. nitric acid the lid to the crucible being in place so as to avoid loss by spattering.
The contents of the crucible was evaporated to dryness over a water bath, heated to constant weight by a Bunsen burner and finally over a blast lamp; the bismuth oxide thus obtained melting without loss in weight. To determine the chlorine in the filtrate, it was first necessary to remove the excess of ammonium sulphide; to do this cadmium nitrate free from arsenic was added, whence cadmium sulphide came down. Copper sulphate was first used, but copper sulphide being soluble in ammonium sulphide, ~~it~~ would not answer. After filtering off the cadmium

sulphide, a little nitric acid and silver nitrate was added; the results obtained in this way, were always 4 or 5 percent low; this error arises from the fact that when ammonium sulphide is used to precipitate the bismuth besides the sulphide, some oxychloride comes down.
It was hoped that by dissolving the double salt in a little nitric acid and then adding a sulphide this trouble could be overcome, but if this is done a large amount of sulphur is thrown out with the bismuth sulphide, which seriously interferes with the determinations of bismuth.
After several months work the following method was found to work satisfactorily.
A weighed portion of the salt not more than .2 gram was treated with water and a little C.P. hydrochloric acid and heated.

nearly to boiling (there should be enough acid to prevent the formation of any basic bismuth salts) sulphuretted hydrogen was then passed in until the supernatant liquid becomes clear; the bismuth sulphide thus formed is filtered off on a quantitative filter and washed with water containing a little hydrogen sulphide, dried, transferred to a weighed porcelain crucible, treated with C.P. nitric acid, evaporated to dryness and heated to a constant weight by a bunsen burner and finally over a blast lamp; bismuth is calculated from the oxide thus obtained.

Besides determining bismuth as the oxide I also determined it directly from the sulphide by filtering this through a gooch crucible, and drying it at 100° to constant weight.

Both of these methods give good results.

To determine the alkali, the filtrate is evaporated to dryness, dissolved again in a little water, filtered into a weighed platinum crucible, evaporated to dryness on a water bath, and then heated for 2 hours at 235° in an air bath and when cool weighed [in the case of caesium it was only heated to about 170°]; the crucible is then heated for a few seconds only over a bunsen burner to a dull red heat and again weighed — the loss here is generally less than .4 mg.
To make the results more accurate the alkali thus determined as the chloride, must be dissolved in a little hot water and filtered, the filter burnt and weighed thus any insoluble matter present, such as silicates from the glass vessels used in evaporation, can be detected, and their weight subtracted from

the weight of the alkali obtained. This method gives good results.

To determine Chlorine — A second sample of the salt is dissolved in several cubic centimeters of C.P. nitric acid, free from chlorine, and water, this is then heated almost to boiling, when about 15 c.cs more of C.P. nitric acid are added — this large excess of acid is necessary to prevent the formation of any basic bismuth salts. — The chlorine is then precipitated by a not too weak solution of silver nitrate. The silver chloride was filtered off in a gooch crucible, first washed with water containing nitric acid and finally with water alone.

The results for chlorine obtained in this way are entirely satisfactory.

## Di-potassium Chloro-bismuthite

## $K_2BiCl_5 \cdot 2H_2O$ $(BiCl_3 \cdot 2KCl \cdot 2H_2O)$

Arppe describes a salt $K_3BiCl_6$ $(BiCl_3 \cdot 3KCl)$ and states when 3 atomic weights of bismuth oxide are dissolved in hydrochloric acid and 3 atomic weights of potassium chloride are added, on evaporation rhombic crystals separate out which on analysis can be shown to have the composition $K_3BiCl_6$.
Following these directions closely I obtained beautiful four sided crystals with two opposite angles cut off, thus presenting a six-sided appearance; the analysis of this salt showed it to have the composition $BiCl_3 \cdot 2KCl \cdot 2H_2O$.
The results obtained are here given.
.1421 gram salt gave .0659 gram $Bi_2O_3$ = .0590 gram Bi

.1472 gram salt gave .2115 gram AgCl = .0522828 gram Cl
.1419 " " " .0417 " KCl = .02187582 " K
.1025 " " lost .0074 gram $H_2O$

| Calculated for $BiCl_3 . 2KCl\ 2H_2O$ | | Found |
|---|---|---|
| Bi | 41.63 | 41.57 |
| K | 15.66 | 15.49 |
| Cl | 35.48 | 35.51 |
| $H_2O$ | 7.20 | 7.18 |

This salt is stable in the air. It does not lose its water of crystallization in a desiccator, but when heated to 100° becomes anhydrous. It dissolves in moderately concentrated hydrochloric acid and can be recrystallized from the same without any change in composition. Its crystallizing power is very great.
All attempts to get the salt with three molecules of potassium chloride were fruitless;

bismuth oxide and potassium chloride are mixed in the exact proportions; one of the former to six of the latter, yet the only salt obtained was $K_2BiCl_5 \cdot 2H_2O$.
Again a large excess of potassium chloride was used and under these conditions potassium chloride crystallizes out first and then the double salt with 2 molecules of the alkali chloride.
Hence I feel justified in asserting that no salt of the formula $K_3BiCl_6$ exists.
Although no description of a double salt of bismuth and potassium chlorides, containing less than two atoms of potassium to one of bismuth, could be found an investigation on this point was made when a salt of the composition $KBiCl_4 \cdot H_2O$ $(BiCl_3 \cdot KCl \cdot H_2O)$ was obtained.

# Mono-Potassium Chloro-bismuthite.
## $KBiCl_4.H_2O$ ($BiCl_3.KCl.H_2O$)

When 2½ atomic weights of bismuth oxide are dissolved in hydrochloric acid and 2 atomic weights of potassium chloride are added and the solution evaporated to a syrupy consistency, there crystallize out beautiful fibre-like needles radiating from centres.
If the solution was not concentrated sufficiently by evaporation the salt $K_2BiCl_5.2H_2O$ invariably crystallized out.
The analysis of this salt dried first by means of a porous plate, and then between filter papers, gave these results:

I
.4109 gram salt gave .2338 gram $Bi_2O_3$ = .2090017 gram Bi
II
.1758 " " " .1005 " $Bi_2O_3$ = .090098 " Bi
III
.1910 " " " .1095 " $Bi_2O_3$ = .0981675 " Bi

I

.1910 gram salt gave .0303 gram KCl = .01904 gram K

II

.1753 " " " .0324 " KCl = .016998 " K.

I

.1752 gram salt gave .2503 gram AgCl = .0618741 gram Cl.

II

.2082 " " " .2976 " AgCl = .0735667 " Cl.

I

.4209 gram salt lost .0190 gram $H_2O$.

.45405 " " " .0167 " $H_2O$.

| Calculated for $BiCl_3 . KCl . H_2O$ | | Found I | II | III |
|---|---|---|---|---|
| Bi | 51.11 | 51.01 | 51.25 | 51.39. |
| K | 9.62 | 9.96 | 9.66 | — |
| Cl | 34.85 | 35.31 | 35.32 | — |
| $H_2O$ | 4.43 | 4.52 | — | 3.67. |

The sample of salt used in analysis III was made from a solution containing a very large excess of bismuth chloride which readily accounts for the high percentage gotten for bismuth and the low percentage

for water.
This salt is stable in the air; it cannot be recrystallized except from a strong solution of bismuth chloride which prevents obtaining the salt entirely free from bismuth chloride. When dissolved in hydrochloric acid on recrystallizing it goes over into $K_2BiCl_5 . 2H_2O$ which appears to be the most stable of the double chlorides of bismuth and potassium.
This salt ($KBiCl_4 . H_2O$) when placed in a desiccator over chloride of calcium loses one-half of its water, while the remainder cannot be driven off below 100°.

| | | |
|---|---|---|
| Weight of the tube + salt (dried on a porous plate) | = | 8.8701 gr. |
| " " " " Empty | = | 8.1592 " |
| " " " salt | = | .7109 " |
| " " " Tube + salt dried to const wgt in desiccator | = | 8.8608 " |
| " " " " + " heated " " " at 105° | = | 8.8515 " |

Loss in weight of salt dried at 105° = =.0186 gr
" " " " " " in a desiccator = .0093 "
percentage of water lost by drying in a desiccator = 2.26

percentage of water in the salt when heated to constant weight at 105° = 4.52 ; thus it appears that in the salt dried over calcium chloride there is ½ molecule of water of crystallization.

A sample of this salt was heated to 140° but the loss in weight indicated the presence of but one molecule of water; when a higher temperature was tried the salt underwent a slight decomposition.

## Potassium-bismuth Alum.
## $KBi(SO_4)_2$ $[K_2SO_4 . Bi_2(SO_4)_3]$

In trying to overcome the difficulties of analyzing the double chloride for chlorine, a method was tried which unexpectedly yielded the salt $KBi(SO_4)_2$.
A weighed quantity of the double chloride of bismuth and potassium was placed in an erlenmeyer flask and treated with concentrated sulphuric acid — the hydrochloric acid set free being conducted into a dilute solution of sodium hydroxide, in this way I hoped to obtain good results on chlorine but failed. However after heating the contents of the flask for several hours, on cooling I noticed fine needle-shaped crystals; on the addition of water they

dissolved and by evaporation were deposited in the needle form as well as in beautiful glistening plates.

The analysis of these crystals show them to have the composition $[K_2SO_4 . Bi_2(SO_4)_3]$ or $KBi(SO_4)_2$ analogous to our ordinary alum $KAl(SO_4)_2 . 12H_2O$. As is to be expected this salt has no water of crystallization being formed in concentrated sulphuric acid.

These are the results obtained:

I
.3478 gram salt gave .1841 gram $Bi_2O_3$ = .1650056 gram Bi
II
.2081 " " " .1109 " $Bi_2O_3$ = .0994218 " Bi

I
.2081 gram salt gave .0416 gram $K_2SO_4$ = .018681 gram K
II
.2388 " " " .0477 " $K_2SO_4$ = .021455 " K

I
.3478 gram salt gave .3672 gram $BaSO_4$ = .151139 gram $SO_4$
II
.1248 " " " .1337 " $BaSO_4$ = .055031 " $SO_4$

| Calculated for $KBi(SO_4)_2$ | Found I | Found II |
|---|---|---|
| Bi 47.36 | 47.44 | 47.77 |
| K 8.91 | 8.99 | 8.98 |
| $SO_4$ 43.72 | 44.10 | 43.72 |

The method of analysis is as follows: dissolve a weighed quantity of the salt in water and hydrochloric acid, add barium chloride to precipitate all the sulphuric acid as barium sulphate — there must be enough hydrochloric acid present to prevent the formation of any basic bismuth salts — filter off into a gooch crucible the barium sulphate, wash first with dilute hydrochloric acid and finally with water dry and weigh, thus calculating the $SO_4$.
In the filtrate the bismuth can be determined if not too much acid is present, or a new sample dissolved in water and hydrochloric acid will suffice, in this

case the determination is exactly the same as with the double chlorides.
To determine the potassium a third sample is dissolved as before, hydrogen sulphide passed in to precipitate the bismuth which is filtered off, and the filtrate evaporated to dryness, redissolved, and filtered into a weighed platinum dish, and again evaporated to dryness, add 3 or 5 drops of sulphuric acid and heat to dryness over a free flame the acid salt first formed being transformed finally in $K_2SO_4$ from the weight of which the potassium is calculated.
This salt possesses the remarkable property of being quite insoluble in cold water, on boiling it however it decomposes into a basic bismuth sulphate of the composition $Bi_2O_2SO_4 \cdot 2H_2O$.
A quantity of the salt $KBi(SO_4)_2$ was boiled in water and the insoluble part filtered off and

dried on a porous plate and analyzed with the following results:

.0896 gram Salt gave .0717 gram $Bi_2O_3$ = .064279 gram Bi

.0896 " " " .0357 " $BaSO_4$ = .014694 " $SO_4$

| Calculated for $Bi_2O_2SO_4 \cdot 2H_2O$ | | Found |
|---|---|---|
| Bi | 71.72 | 71.74 |
| $SO_4$ | 16.55 | 16.39 |

In the filtrate was found potassium and sulphuric acid hence the decomposition may be expressed thus

$$2BiK(SO_4)_2 + 2H_2O = Bi_2O_2SO_4 + K_2SO_4 + 2H_2SO_4 \text{. or}$$
$$= Bi_2O_2SO_4 + 2HKSO_4 + H_2SO_4 \text{.}$$

## Potassium-antimony Alum.

By analogous methods of work I hoped to have obtained a double sulphate of antimony

and potassium as well as one of arsenic and potassium, thus making more complete a series of double salts, comparable with the well known alums.
I first made the double chloride of antimony and potassium, then boiled it with concentrated sulphuric acid for eight hours, on cooling well crystallized needles separated out, on the addition of water instead of behaving like the corresponding bismuth compound, it immediately broke down into basic antimony sulphate.
A second sample of the double chloride was heated for two days with concentrated sulphuric acid, on cooling the same crystalline mass appeared, and on the addition of water acted as before.
A third sample was heated for eight hours with concentrated sulphuric acid, and in-

stead of trying to recrystallize the mass, the excess of acid was poured off, and the salt placed on a porous plate to dry; by this treatment the salt absorbed moisture from the air and gradually changed into basic antimony sulphate: It was next placed in a vacuum over soda lime and caustic potash; at the end of one month it was fairly dry, although the excess of acid had not entirely disappeared.
An analysis was made which gave 17.9 per cent antimony and .78 per cent potassium or a ratio between the atoms of antimony and potassium of .498 to .0669 instead of 1 to 1.
Further investigation of this salt was given up as it was found impossible to get the salt pure enough for sharp analysis. However the work done tends to show the

non-existence of a salt of the composition $KSb(SO_4)_2$ analogous to $KBi(SO_4)_2$.
This is not surprising since antimony is a much weaker base than bismuth and has greater acid properties, hence we can trace a gradual gradation:- in ordinary alum $KAl(SO_4)_2$ we have great stability especially toward water, with bismuth-potassium sulphate we find a tendency for it to break down on boiling with water, while in the case of antimony no double salt $KSb(SO_4)_2$ can be obtained.
Arsenic having still greater acid properties will probably act like antimony and show no signs of forming a double sulphate.
It would be interesting to see whether an analogous compound containing boron could be made.

# Tri-rubidium Chloro-bismuthite

$Rb_3BiCl_6$ ($BiCl_3 \cdot 3RbCl$)

The only work on the double chlorides of bismuth and rubidium was done by Richard Godeffroy[9] who published his results in 1875[10], in which he describes as well as gives complete analyses of the salt $Rb_6BiCl_9$ ($BiCl_3 \cdot 6RbCl$) which forms a marked exception to the law regarding the constitution of the double halides. As many of the salts discovered by Godeffroy, which have appeared as exceptions to the law, have by subsequent work been shown not to exist, it was deemed advisable to carefully investigate this double chloride and determine first, whether or not it had the composition $Rb_6BiCl_9$,

9. Berichte 8, 9

secondly to ascertain whether by the further addition of bismuth or rubidium chloride a salt could be formed with a greater or less percentage of bismuth, similar to the salts obtained in the case of potassium.

His description of the salt is briefly thus:
"By evaporation of a hydrochloric acid solution of bismuth chloride and rubidium chloride beautiful crystals separate out."
His analysis as follows:

| | | | | |
|---|---|---|---|---|
| .1535 gram salt gave | .191 gram | $AgCl$ | = .0473 gram | $Cl$ |
| .1535 " " " | .036 " | $Bi_2O_3$ | = .03088* " | $Bi$ |
| .423 " " " | .707 " | $Rb_2PtCl_6$ | = .2077 " | $Rb$ |

| Calculated for $BiCl_3 . 6RbCl$ | | Found |
|---|---|---|
| Bi | 20.00 | 20.120 |
| Cl | 30.72 | 30.803 |
| Rb | 49.28 | 49.110 |

* A miscalculation, should be .032274 gram Bi

In order to give the best chance for the formation of this salt; rubidium chloride was dissolved in a little cold dilute hydrochloric acid and drop by drop to this was added a hydrochloric acid solution of bismuth chloride: thus the presence of a large excess of rubidium chloride gave the most favorable opportunity for the formation of a salt containing six atoms of rubidium if formed at all.
On the addition of the slightest quantity of bismuth chloride, a voluminous crystalline precipitate was immediately formed, no evaporation being necessary.
Godeffroy states that there is no precipitate formed when solutions of bismuth and rubidium chlorides are mixed.
A small quantity of this precipitate was removed, dried on a porous plate and

analyzed with the following results.

.1884 gram salt gave .0644 gram $Bi_2O_3$ = .057734 gram Bi
.1427 " " " .0761 " RbCl = .053772 " Rb
.1999 " " " .2551 " AgCl = .0630607 " Cl

| | Calculated for $BiCl_3 . 3RbCl$ | Found |
|---|---|---|
| Bi | 30.72 | 30.65 |
| Rb | 37.84 | 37.68 |
| Cl | 31.42 | 31.54 |

On heating a sample of this salt for 2 hours at 110° it lost in weight but slightly giving only .2 per cent loss, which was probably due to incomplete drying.
Thus this analysis of the precipitate goes to show that it has the composition $Rb_3BiCl_6$ ($BiCl_3 . 3RbCl$) and not $Rb_6BiCl_9$ ($BiCl_3 . 6RbCl$).
Another portion of the precipitate was dissolved in moderately concentrated hydrochlo-

ric acid and the solution evaporated, when beautiful transparent crystals separate out, which on the addition of concentrated hydrochloric acid become opaque. These crystals are diamond-shaped, very regular in form, and similar to those of the potassium salt $K_2BiCl_5 . 2H_2O$, but without the opposite angles cut off. The crystallizing power of this salt is weak and consequently the crystals are of small size but quite uniform.

These crystals were dried on porous plates and then pressed between drying paper and on analysis gave the following results:

I
.1552 gram salt gave .0536 gram $Bi_2O_3$ = .048042 gram Bi

II
.2132 " " " .0734 " $Bi_2O_3$ = .065803 " Bi

I
.1835 gram salt gave .0985 gram RbCl = .06961 gram Rb

II
.1609 " " " .0860 " RbCl = .060767 " Rb

I
.1349 gram salt gave .1777 gram AgCl = .043927 gram Cl
II
.2093 " " " .2670 " AgCl = .066002 " Cl

| | Calculated for $BiCl_3 \cdot 3RbCl$ | Found I | Found II |
|---|---|---|---|
| Bi | 30.72 | 30.97 | 30.86 |
| Rb | 37.84 | 37.93 | 37.76 |
| Cl | 31.42 | 31.49 | 31.53 |

The recrystallized precipitate when heated to 110° for 2 hours lost but slightly in weight, showing there is no water of crystallization in the salt: the decrease being due to insufficient drying, probably the presence of a little hydrochloric acid.
This salt dissolves undecomposed in dilute hydrochloric acid, and on evaporation of the solution always crystallizes out in the same form. Water decomposes it with the formation of basic bismuth chloride and rubid-

um chloride.

Other attempts to obtain the salt of Godeffroy were made by using a cold concentrated solution of rubidium chloride, and a cold dilute solution of bismuth chloride, also hot solutions were used, but without any success – the salt crystallizing out always being $Rb_3BiCl_6$.

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## $Rb_{23}Bi_{10}Cl_{53}$ (?)

($10BiCl_3 . 23RbCl$)

Since with compounds of stannous chloride and potassium chloride, we get more than one salt, namely $SnCl_2.KCl\,H_2O$ [10] and $SnCl_2 . 2KCl . 2H_2O$, and with bismuth

10. "Stannous Double Halide Salts" a Thesis by Geo. M. Richardson for degree of Doctor of Philosophy. Johns Hopkins University. 1890

chloride and potassium chloride we find $BiCl_3\,2KCl.2H_2O$" and $BiCl_3\,KCl.H_2O$ so it was thought possible to obtain other double chlorides of bismuth and rubidium, containing a greater percentage of bismuth in the molecule by the addition of bismuth chloride to a solution of the salt $Rb_3BiCl_6$ in hydrochloric acid."

When bismuth oxide and rubidium chloride are mixed in the proportion of one molecular weight of the former to two (2) of the latter and the mixture dissolved in dilute hydrochloric acid and evaporated, there separates out a salt crystallizing in most varied forms, resembling shapes of snow crystals, which however on standing change and assume the form of hexagonal plates.

These crystals are transparent, quite small

11 This Thesis. page 5

but very regular in habit.
This salt was obtained in such small quantities that purification by crystallization was impossible; in fact when recrystallized from hydrochloric acid it passes over into the compound $Rb_3BiCl_6$; it can however be recrystallized from a solution of bismuth chloride.
An analysis of this salt, sharp enough to give a decided formula could not be made, owing to its probable impurity due to the impossibility of purifying it by repeated crystallization
The following results were obtained:

I
.1563 gram salt gave .0603 gram $Bi_2O_3$ = .0540589 gram Bi
II
.2483 " " " .0973 " $Bi_2O_3$ = .0872299 " Bi

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I
.1563 gram salt gave .0719 gram RbCl = .0508045 gram Rb
II
.2483 " " " .1138 " RbCl = .0814909 " Rb

I
.1525 gram salt gave .1956 gram AgCl = .0483523 gram Cl
II
.1992 " " " .2551 " AgCl = .0630607 " Cl

| Calculated for $10BiCl_3 . 23RbCl$ | | Found I | Found II |
|---|---|---|---|
| Bi | 35.11 | 34.58 | 35.17 |
| Rb | 33.17 | 32.50 | 32.83 |
| Cl | 31.72 | 31.74 | 31.66 |

From analysis I the calculated ratio between the bismuth and rubidium atoms is 1 to 2.296 and from analysis II, 1 to 2.275 and the formula which would seem most probable, in view of these facts is $Rb_{23}Bi_{10}Cl_{53}$ or $10BiCl_3 . 23RbCl$. Were it not for certain facts along a similar line of work undertaken by Mr. C. E. Saunders, under the direction of Prof. Remsen the [illegible] formula would seem highly improbable. This gentleman working on the double chlorides of antimony and

rubidium, obtained a salt, crystallizing in the same form, the analysis of which gave a ratio between the bismuth and rubidium atoms of 1 to 2.296. (mean of three analyses).
The one fact which goes to establish these results as most exact is that this double salt of antimony and rubidium can be recrystallized from hydrochloric acid <u>without change of composition</u>, and it is into this salt that all double chlorides of antimony and rubidium change, when subjected to recrystallization from dilute hydrochloric acid.
The results which Mr Saunders obtained were from the analyses of the salt which had been purified by recrystallization five times.
Since bismuth is so closely related to anti-

mony and the work on the double chloride of the latter with rubidium shows the existence of a salt of the probable composition $10SbCl_3.23RbCl$, it is not surprising that a similar compound of bismuth should be formed; from this fact and the results actually obtained by me in the analysis of the salt above described, I feel justified in assigning to this compound the formula $Rb_{23}Bi_{10}Cl_{53}$.
With the existence of this and the similar antimony salt the view that "halogen atoms can play the same part as linking oxygen atoms" must be slightly modified." This modification is fully set forth in Mr Saunders's dissertation for the degree of Doctor of Philosophy. Johns Hopkins University, 1891".
The view this gentleman takes is that in

the compound $10SbCl_3 . 23RbCl$ some of the chlorine atoms may be assumed to be in groups of three with three free valencies, and that with this assumption not only can these two compounds be explained, and brought into harmony with the other double halides, but the compound $CuCl . 2KCl$ which has always stood out as a marked exception finds a partial explanation: according to this view it would have this structure

$$CuCl \lt \begin{matrix} Cl-K \\ Cl-K \end{matrix}$$

This salt ($Rb_{23}Bi_{10}Cl_{53}$) dissolves to a clear solution in dilute hydrochloric acid, from which on partial evaporation, there crystallizes out the salt $Rb_3BiCl_6$, which appears to be the one that these elements always assume under ordinary conditions. In water this salt is decomposed with the formation of basic bismuth chloride.

# Mono-rubidium Chloro-bismuthite
## $RbBiCl_4 . H_2O$ ($BiCl_3 . RbCl . H_2O$)

Besides the compounds $Rb_3BiCl_6$ ($BiCl_3$ 3 $RbCl$) and $Rb_{23}Bi_{10}Cl_{53}$ ($10 BiCl_3 . 23 RbCl$) another was obtained, which in all probability corresponds to the mono-potassium chloro-bismuthite and has the composition $RbBiCl_4 . H_2O$. It was found that when 2½ molecular weights of bismuth oxide were dissolved in concentrated hydrochloric acid, and 2 molecular weights of rubidium chloride were added and the solution evaporated to a syrupy consistency, after a time white hair-like crystals formed and finally the contents of the vessel became almost solid; the beaker in which the salt was formed was turned on its side and the liquid al-

allowed to drain off, after which the crystals were transferred to a porous plate and finally dried between filter papers. If the evaporation of the solution be stopped before the liquid becomes sufficiently concentrated for the formation of these needle-like crystals, there always separates out crystals of the compound $10 BiCl_3 . 23 RbCl$, while on the contrary should the evaporation be carried beyond the point at which the hair-like crystals first form these needles although they are formed do not appear separate but seem to start from points and form themselves into a solid mass radiating from these points as centres.
The rubidium chloride used in this experiment was found on analysis to be slightly impure, containing probably a slight trace of caesium.

.2522 gram $RbCl$ gave .2806 gram $AgCl$ = .07084 gram $Cl$ = 28.09%. Theoretical percent of $Cl$ in $RbCl$ = 29.34

The conditions under which this double salt is formed — in a very concentrated solution of bismuth chloride — give little opportunity for the purification of the salts used. Were this salt formed in dilute acid solution any impurity present in the rubidium chloride might be removed by the difference in solubility of the double salts produced, but being formed in such concentrated solutions where bismuth chloride is present in such large excess, and where it appears as if all of both constituents present enter into combination, it is not surprising that if caesium is the impurity in the rubidium chloride, that it would be carried along by both constituents and enter into combination.

This is certainly the reason why the analyses of the salt do not correspond to any simple formula although its similar method of formation and appearance to the potassium salt of the composition $KBiCl_4 \cdot H_2O$, strongly impresses me with the belief that it most certainly has the composition $RbBiCl_4 \cdot H_2O$. The results of the analyses of three different samples are as follows:

Sample A

I
.1275 gram salt gave .0622 gram $Bi_2O_3$ = .055762 gram Bi

II
.1223 " " " .0598 " $Bi_2O_3$ = .0536107 " Bi

Sample B

I
.1315 gram salt gave .0743 gram $Bi_2S_3$ = .060340 gram Bi

II
.1263 " " " .0643 " $Bi_2O_3$ = .0576449 " Bi

III
.4108 " " " .2315 " $Bi_2S_3$ = .1880243 " Bi

Sample C

I
.2250 gram salt gave .1212 gram $Bi_2S_3$ = .0984383 gram Bi

II
.1666 " " " .0940 " $Bi_2S_3$ = .0763468 " Bi

Sample A

I

.1275 gram salt gave .0394 gram RbCl = .02784 gram Rb.

II

.1223 " " " .0379 " RbCl = .02678 " Rb

Sample B

I

.1315 gram salt gave .0408 gram RbCl = .028829 gram Rb

II

.1263 " " " .0408 " RbCl = .028829 " Rb

Sample C

II

.1666 gram salt gave .0520 gram RbCl = .036842 " Rb.

---

Sample A

I

.1204 gram salt gave .1564 gram AgCl = .038652 gram Cl

II

.1829 " " " .2379 " AgCl = .0588088 " Cl

Sample B

I

.1203 gram salt gave .1562 gram AgCl = .0386126 gram Cl

II

.1739 " " " .2261 " AgCl = .055891 " Cl

Sample C

I

.2189 gram salt gave .2848 gram AgCl = .0704025 gram Cl

II

.2578 " " " .3350 " AgCl = .082812 " Cl

---

Sample A
I
.4347 gram salt lost .0110 gram $H_2O$ heated for 2 hrs. 105°

Sample B
I
.4151 gram salt lost .0043 gram $H_2O$ heated for 2 hrs. 105°

Sample C
I
.4085 gram salt lost .0067 gram $H_2O$ heated for 2 hrs. 105°
II
.1957 " " " .00295 " $H_2O$ " " 2 " 105°

| Calculated for | | | Found | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Sample A | | Sample B | | | Sample C | |
| | $RbBiCl_4 \cdot H_2O$ : | $RbBiCl_4$ | I | II | I | II | III | I | II |
| Bi | 45.89 | 47.79 | 43.73 | 43.83 | 45.89 | 45.64 | 45.77 | 45.78 | 45.82 |
| Rb | 18.84 | 19.62 | 21.83 | 21.89 | 21.79 | 22.54 | — | — | [illegible] |
| Cl | 31.29 | 32.58 | 32.10 | 32.17 | 32.09 | 32.14 | — | 32.16 | 32.11 |
| $H_2O$ | 3.97 | | 2.53 | — | 1.03 | — | — | 1.64 | 1.50 |

The bismuth in analyses I and III sample B and I and II sample C was determined as the sulphide - while that in I and II sample A and II sample B was calculated from the oxide.

It will be seen on comparing the results cal-

culated for $RbBiCl_4 \cdot H_2O$ with the percentages found that while there is a discrepancy in the case of rubidium and water, the percentages for bismuth and chlorine are close, and as I previously stated, on account of the great similarity between it and the compound $KBiCl_4 \cdot H_2O$ I am satisfied to state that if the rubidium chloride had been perfectly pure the results obtained on analysis would have been extremely close to the calculated percentages for $RbBiCl_4 \cdot H_2O$. The salt, as is the case with the other salts of bismuth and rubidium, is decomposed by water but yields a clear solution when treated with dilute hydrochloric acid, from which on slight evaporation there separates the salt $BiCl_3 \cdot 3RbCl$.

All efforts to obtain salts composed of bismuth and rubidium chlorides, other than have

have been described, have proved fruitless. From these facts it appears to follow that the salt $BiCl_3 \cdot 6RbCl$, described by Godeffroy does not exist, and cannot under the most favorable conditions — in the presence of a large excess of rubidium chloride — be formed.

## Caesium-bismuth Chlorides.

As with rubidium so with caesium Godeffroy[12] describes a salt of the composition $BiCl_3 \cdot 6CsCl$ and to determine whether such a compound exists, was the following work undertaken. The caesium chloride

12 Berichte 8, 9

for this investigation was obtained from the factory of Theodor Schuchardt, Görlitz Ger. On analysis it was found to be very impure, containing most probably rubidium and potassium; so before beginning the investigation of this double chloride, it was necessary to purify this salt.
The method[13] employed depended on the difference in solubility of the double salts of antimony-rubidium chloride, and antimony-caesium chloride, the former being soluble in concentrated hydrochloric acid, the latter not. The caesium chloride was dissolved in moderately concentrated hydrochloric acid and a solution of antimony chloride in hydrochloric acid added until it ceased forming a precipitate; this was allowed to stand until clear when the supernatant liquid was poured off; concentrated hydrochloric acid was

13 Annalen 181, 183

added to the precipitate, in which case any rubidium-antimony chloride present would dissolve. This liquid was poured off, when the precipitate remaining should contain only caesium-antimony chloride. This was dissolved in <u>hot</u> concentrated hydrochloric acid then hydrogen sulphide was passed in, for a <u>long</u> time as the large quantity of acid used to dissolve this salt prevents the complete precipitation of the antimony at once. The antimony sulphide was filtered off and the filtrate (containing the caesium chloride was evaporated to dryness in a <u>platinum dish</u>. If a glass or porcelain vessel is used some alkali from the glass will be dissolved. To drive off the last trace of hydrochloric acid, it was heated to 130° in an air bath. The caesium chloride thus treated was found to be much purer than that

with which I started, yet a second purification seemed advisable; the result of which gave me a small quantity of the salt which analyzed as follows:

.1711 gram CsCl gave .1470 gram AgCl = .0363384 gram Cl = 21.23 per cent. Theoretical percentage of Cl in caesium chloride = 21.05. This is probably as pure as caesium chloride can be obtained by this method: the quantity of the salt would not warrant a third purification.

Godeffroy[4], in his description of the salt $BiCl_3.6CsCl$ says he obtained, by mixing solutions of bismuth and caesium chlorides in hydrochloric acid, a precipitate which is difficultly soluble in hydrochloric acid, and his analysis is as follows:

.900 gram salt gave .801 gram AgCl = .213 gram Cl.
.900 " " " .154 " $Bi_2O_3$ = .138 " Bi
.550 " " " .788 " $Cs_2PtCl_6$ = .3095 " Cs.

4 Berichte 8 9

| Calculated for $BiCl_3 \cdot 6\,CsCl$ | | Found |
|---|---|---|
| Cl | 24.10 | 23.67 |
| Bi | 15.68 | 15.87 |
| Cs | 60.22 | 60.09 |

Following these directions for making this salt, to a saturated solution of Caesium Chloride in dilute hydrochloric acid was added drop by drop a solution of bismuth chloride when a voluminous precipitate difficultly soluble was formed. A close examination of the precipitate shows the presence of two distinct kinds of crystals.

Desiring to follow Godeffroy's direction and obtain his salt, this precipitate as it stood was analyzed.

A sample of it dried on a porous plate and finally between filter paper, gave the results.

I .171 gram salt gave .0701 gram $Bi_2S_3$ = .0569352 gram Bi

II .081 " " " .0782 " $Bi_2S_3$ = .063514 " Bi

I
.171 gram salt gave .0862 gram $CsCl$ = .0680549 gram $Cs$
II
.1881 " " " .0947 " $CsCl$ = .0747656 " $Cs$

I
.1534 gram salt gave .1693 gram $AgCl$ = .04185 gram $Cl$
II
.1507 " " " .1671 " $AgCl$ = .04307 " $Cl$

| | Calculated for | | Found | |
|---|---|---|---|---|
| | $BiCl_3 . 2CsCl$ | $BiCl_3 . 6CsCl$ | I | II |
| Bi | 31.93 | 15.68 | 33.29 | 33.76 |
| Cs | 40.84 | 60.22 | 39.79 | 39.74 |
| Cl | 27.22 | 24.10 | 27.28 | 27.41 |

These results show that the precipitate is most probably a mixture as it corresponds to no single salt but having a composition somewhat near $BiCl_3 . 2CsCl$; however the results are decidedly off for the salt described by Godeffroy which cannot under any consideration be formed. The salt which he analyzed and to which he attributed the formula $BiCl_3 . 6CsCl$ must have been very impure, containing a large quantity of caesium

as the impurity.
This precipitate dissolves easily in warm dilute hydrochloric acid one of the salts with apparently more ease than the other, so as one would expect it is quite an easy matter to separate and obtain them in pure condition by recrystallization. On evaporation of a solution of the precipitate in hydrochloric acid, the more compact looking crystals, which settled to the bottom of the precipitate formed yellowish elongated pyramids, while the others, which are the more easily soluble assume a flaky appearance (these are white or colorless). After separation each lot was recrystallized twice from dilute hydrochloric acid, and although but a small quantity of each was obtained they appeared quite pure and gave excellent results on analysis.

# $Cs_3Bi_2Cl_9$

$2BiCl_3 \cdot 3CsCl$.

That part of the precipitate, formed by mixing solutions of bismuth and caesium chlorides in hydrochloric acid, which on recrystallization forms elongated pyramids, yellow in color, has the composition $Cs_3Bi_2Cl_9$, as shown by the following analysis.

.1587 gram salt gave .072 gram $Bi_2S_3$ = .0584784 gram Bi
.1587 " " " .0708 " CsCl = .0558966 " Cs
.1390 " " " .1586 " AgCl = .0392059 " Cl

| | Calculated for $2BiCl_3 \cdot 3CsCl$ | Found |
|---|---|---|
| Bi | 36.68 | 36.84 |
| Cs | 35.18 | 35.22 |
| Cl | 28.13 | 28.20 |

This salt on treatment with water decomposes with the formation of oxychloride of bismuth and caesium chloride: in acid

dilute hydrochloric acid it is difficultly soluble, but dissolves readily when warmed. With the formation of this salt is the similarity between the elements bismuth and antimony again shown, as the chloride of the latter with caesium chloride only forms a salt of the composition $Cs_3Sb_2Cl_9$

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## Tri-caesium Chloro-bismuthite.

$Cs_3BiCl_6$ $(BiCl_3 \cdot 3CsCl)$

That part of the precipitate which crystallizes in thin transparent plates has the composition $Cs_3BiCl_6$

The results obtained on analysis of this salt are as follows:

I
.189 gram salt gave .0376 gram $Bi_2S_3$ = .0305387 gram Bi.
II
.1730 " " " .0544 " $Bi_2S_3$ = .044806 " Bi

II
.1730 gram salt gave .1063 gram CsCl = .0839238 gram Cs.

I
.08.. gram salt gave .0860 gram AgCl = .0212592 gram Cl

| | Calculated for $BiCl_3 \cdot 3CsCl$ | Found I | II |
|---|---|---|---|
| Bi | 25.37 | 25.58 | 25.53 |
| Cs | 48.67 | — | 48.51 |
| Cl | 25.95 | 26.08 | — |

Through an accident the determination of caesium in analysis I was lost.
The behavior of this salt is much like that of the composition $Cs_3Bi_2Cl_9$; it is difficultly soluble in dilute hydrochloric acid cold but when warmed dissolves easily.

With the double chlorides of rubidium and

caesium with bismuth, it was so difficult to obtain the compounds well crystallized that an investigation into their crystallographic properties was not undertaken.

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## Conclusion.

The principal results of this investigation are these:

I Of the three chloro-bismuthites of potassium only the one described by Jacquelaine exists ($BiCl_3 . 2KCl . 2H_2O$)[15]; while one of the composition $BiCl_3 . KCl . H_2O$, not described in the literature, can be formed under certain conditions.

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15 Ann. chim. phys. 66, 113.

II No salt of the composition $Rb_6BiCl_9$ exists, but from the chlorides of bismuth and rubidium the following three salts can be formed

$Rb_3BiCl_6$ $Rb_{23}Bi_{10}Cl_{53}$ $RbBiCl_4.H_2O$

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III The salt, to which Godeffroy ascribes the the composition $BiCl_3.6CsCl$ is a mixture of the two salts $Cs_3BiCl_6$ ($BiCl_3.3CsCl$) and $Cs_3Bi_2Cl_9$ ($2BiCl_3.3CsCl$), and cannot under any possible circumstance be formed

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IV All double chlorides of bismuth with the alkali metals are decomposed by water.

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V As the atomic weight of the alkali in combination with bismuth increases, the amount of water of crystallization decreases thus: $BiCl_3.2NaCl.3H_2O$, $BiCl_3.2KCl.2H_2O$, $BiCl_3.RbCl.H_2O$, $BiCl_3.3CsCl$.

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II Of the exceptions to the law of combination in double halides only two now exist CuCl.2KCl and CdCl$_2$.4KCl. all work done on these two compounds show their composition to be expressed by these formulae.

# Biographical Sketch

The author of this dissertation, Charles Pliny Bingham, was born February 3, 1867 in Baltimore Maryland. He prepared for college at the "University School for Boys" in that city. In the fall of 1885 he entered the Johns Hopkins University as an undergraduate; after following the course in Chemistry & Physics graduated with the degree of Bachelor of Arts in June 1888.
In the following fall he entered the graduate department where he has pursued the study of Chemistry, with mineralogy and geology as subsidiary subjects.